

SPECIFICATION

TRIMERIZATION CATALYST FOR OLEFIN

Technical Field

5 The present invention relates to a trimerization catalyst for olefin, and a process for trimerizing an olefin using the catalyst.

Background Art

10 As a process of using a tantalum compound to selectively trimerize an olefin, in particular, ethylene, there are disclosed in USP No. 6344594 and J. Am. Chem. Soc., 2001, 123, 7423 a catalyst composition comprising a tantalum compound and an alkylating agent. As the alkylating agent, disclosed are tetramethyltin, 15 tetraethyltin, allyltriphenyltin, tetra-n-butyltin, tetraphenyltin, dimethylzinc, diethylzinc, trimethylaluminum, triethylaluminum, methylaluminoxane, dimethylaluminum chloride, methyl lithium, n-butyllithium, tert-butyllithium, phenyllithium, methylmagnesium bromide, and the like. However, 20 the ethylene-trimerizing process using the catalyst composition disclosed in the above-mentioned documents has a problem in that the catalytic activity thereof is not necessarily sufficient.

Disclosure of the Invention

25 According to the invention, a catalyst having a good catalytic activity can be obtained, and an olefin can be effectively trimerized by use of this catalyst.

 Accordingly, the invention provides:

 an olefin-trimerizing catalyst comprising

(A) a tantalum compound, and

(B) an organic metal compound, wherein the organic metal compound (B) comprises at least one group selected from the group consisting of the following (1) to (5):

5 (1) a branched or cycloalkyl-substituted primary alkyl group having 4 to 15 carbon atoms,

 (2) an aryl-substituted primary alkyl group having 7 to 15 carbon atoms,

 (3) a 3-alkenyl group having 4 to 15 carbon atoms,

10 (4) a secondary alkyl group having 3 to 15 carbon atoms which may be substituted with an aryl group or a cyclic alkyl group having 3 to 15 carbon atoms, and

 (5) a secondary alkenyl group having 4 to 15 carbon atoms; and a process for trimerizing an olefin in the presence of the
15 above-mentioned olefin-trimerizing catalyst.

Best Mode for Carrying Out the Invention

 The tantalum compound (A) in the invention include a tantalum halide, an alkoxide tantalum and the like. Preferred
20 is a tantalum halide, and is more preferably tantalum (V) fluoride, tantalum (V) chloride, tantalum (V) bromide, tantalum (V) iodide, and the like.

 A description will be made to the groups (1) to (5) which constitute the organic metal compound (B) used in the invention
25 are described.

 (1) Specific examples of the branched or cycloalkyl-substituted primary alkyl group having 4 to 15 carbon atoms include isobutyl, 2-methylbutyl, 2-ethylbutyl, 2,2-dimethylpropyl, isopentyl, 2-methylpentyl, isohexyl,

2-methylhexyl, 2-ethylhexyl, cyclopentylmethyl, and cyclohexylmethyl groups. Preferred are the isobutyl, 2-methylbutyl, 2-methylpentyl, cyclopentylmethyl, and cyclohexylmethyl groups. More preferred is the isobutyl group.

5 (2) Specific examples of the aryl-substituted primary alkyl group having 7 to 15 carbon atoms include benzyl, 2-phenylethyl, and 2-phenylpropyl groups. Preferred is the 2-phenylethyl group.

 (3) Specific examples of the 3-alkenyl group having 4 to
10 15 carbon atoms(homo-allyl type group) include 3-butenyl, 2-methyl-3-butenyl, and 3-methyl-3-butenyl groups. Preferred are primary or secondary 3-alkenyl groups having 4 to 15 carbon atoms, a specific example thereof being the 3-butenyl group.

 (4) Specific examples of the a secondary alkyl group having
15 3 to 15 carbon atoms which may be substituted with an aryl group or a cyclic alkyl group having 3 to 15 carbon atoms include isopropyl, sec-butyl, 2-(3-methyl)-butyl, 2-pentyl, cyclopentyl, cyclohexyl, and 1-phenylethyl groups. Preferred are the isopropyl, sec-butyl, cyclopropyl, cyclopentyl,
20 cyclohexyl, and 1-phenylethyl groups.

 (5) Specific examples of the secondary alkenyl group having 4 to 15 carbon atoms include 1-methyl-2-propenyl, 3-(1-pentenyl), 3-(4-methyl-1-pentenyl), and 1,2-dimethyl-2-propenyl groups. Preferred is the 1-methyl-2-propenyl group.

25 Of the above, the following are more preferred as the organic metal compound (B) comprising at least one group selected from the group consisting of isopropyl, isobutyl, sec-butyl, 3-butenyl, cyclopentylmethyl, cyclohexylmethyl, 1-phenylethyl, and 2-phenylethyl groups. Most preferred is a compound

comprising isobutyl group.

The organic metal compound (B) in the invention includes, as examples thereof, the following alkylating agents.

Specific examples of the organic metal compound (B) include, for example, alkyllithium, alkylmagnesium halides, alkylaluminum, alkylaluminumoxane, and alkyltin.

Specific examples of the alkyllithium include isopropyllithium, sec-butyllithium, isobutyllithium, cyclopentyllithium, 2,2-dimethylpropyllithium, cyclohexyllithium, 1-phenylethyllithium, and 2-phenylethyllithium. Preferred are isopropyllithium, sec-butyllithium, isobutyllithium and the like.

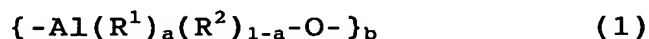
Specific examples of the alkylmagnesium halides include isopropylmagnesium halides, cyclopentylmagnesium halides, 2,2-dimethylpropylmagnesium halides, cyclohexylhalides, 1-methyl-2-propenylmagnesium halides, 2-phenylethylmagnesium halides, 3-butenylmagnesium halides, cyclopropylmagnesium halides, sec-butyilmagnesiumhalides, isobutyilmagnesiumhalides, 2-ethylhexylmagnesium halides, and 2-ethylbutylmagnesium halides. Preferred are isopropylmagnesium halides, cyclopentylmagnesium halides, cyclohexylhalides, 2-phenylethylmagnesium halides, 3-butenylmagnesium halides, sec-butyilmagnesium halides, isobutyilmagnesium halides and the like. Preferred are the isopropylmagnesium halides, sec-butyilmagnesium halides, and isobutyilmagnesium halides. Examples of the halides in the alkylmagnesium halides above include chlorine, bromine, iodine and the like.

Specific examples of the alkylaluminum include triisopropylaluminum, triisobuytlaluminum,

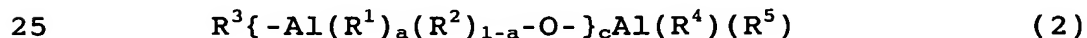
tri-sec-butylaluminum, tricyclopentylaluminum,
tri(2,2-dimethylpropyl)aluminum, tricyclohexylaluminum,
diisopropylaluminum chloride, isopropylaluminum dichloride,
diisobutylaluminum chloride, isobutylaluminum dichloride,
5 di-sec-butylaluminum chloride, sec-butylaluminum dichloride,
and diisobutylaluminum hydride. Preferred are
triisopropylaluminum, triisobutylaluminum,
tri-sec-butylaluminum, diisobutylaluminum chloride,
isobutylaluminum dichloride, and diisobutylaluminum hydride.

10 More preferred is triisobutylaluminum.

Examples of the alkylaluminumoxane include cyclic
aluminumoxane having a structure represented by the following
formula (1):



15 wherein R^1 represents a hydrogen atom or a hydrocarbon having
1 to 8 carbon atoms, R^2 represents a primary alkyl group which
has a branch and has 4 to 15 carbon atoms, a primary alkyl group
which has an aryl group as a substituent and has 7 to 15 carbon
atoms, a homo-allyl group which has 4 to 15 carbon atoms, a
20 secondary alkyl group which has 3 to 15 carbon atoms, or a secondary
alkenyl group which has 4 to 15 carbon atoms, a represents a
numerical value of 0 or more and less than 1, and b represents
an integer of 2 or more; or linear aluminumoxane having a structure
represented by the formula (2):



25 wherein R^1 , R^2 and a have the same meanings as described above,
 R^3 , R^4 and R^5 , which may be the same or different, each represents
a hydrogen atom, or a hydrocarbon group having 1 to 8 carbon
atoms, and c represents an integer of 1 or more.

Specific examples of the hydrocarbon having 1 to 8 carbon atoms for R^1 , R^3 , R^4 or R^5 include methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl and tert-butyl groups. Preferred are the methyl, and isobutyl groups.

5 In R^2 , specific examples of the primary alkyl group which has a branch and has 4 to 15 carbon atoms, the primary alkyl group which has an aryl group as a substituent and has 7 to 15 carbon atoms, the homo-allyl group which has 4 to 15 carbon atoms, the secondary alkyl group which has 3 to 15 carbon atoms, or
10 the secondary alkenyl group which has 4 to 15 carbon atoms, include the substituents described above. Preferred is isobutyl group. "a" represents a numerical value of 0 or more and less than 1. "b" is an integer of 2 or more, and "c" represents an integer of 1 or more. Preferably, b is an integer of 2 to 40 and c is
15 an integer of 1 to 40.

Specific examples of the aluminoxane include a modified methylaluminoxane (aluminoxane wherein methyl groups in methylaluminoxane are partially substituted with isobutyl groups), and isobutylaluminoxane.

20 The above-mentioned aluminoxane can be produced by various methods, which are not particularly limited. The aluminoxane can be produced in accordance with a known method. For example, the aluminoxane can be produced by bringing water into contact with a solution wherein a trialkylaluminum (such as
25 triisobutylaluminum) is dissolved in a suitable organic solvent (such as benzene or an aliphatic hydrocarbon). Furthermore, an example of the known method is a method of bringing a trialkylaluminum (such as triisobutylaluminum) into contact with a metal salt containing crystal water (such as copper sulfate

hydrate). A commercially available product may be used. Specific examples of the alkyltin include tetraisopropyltin, isopropyltrimethyltin, tetraisobutyltin, tetra(2,2-dimethylpropyl)tin, diisobutyltin dichloride, 5 tetra-sec-butyltin, and tetracyclohexyltin. Preferred are tetraisopropyltin, tetraisobutyltin, tetra-sec-butyltin, and the like.

The above-mentioned alkylating agents may be used alone or in the form of a mixture of two or more thereof.

10 The olefin-trimerizing catalyst of the invention, which comprises a tantalum compound and an alkylating agent, can be prepared by bringing the tantalum compound and the alkylating agent into contact with each other. The method for the preparation is not particularly limited. For example, the 15 catalyst can be prepared by bringing the tantalum compound and the alkylating agent into contact with each other in a solvent, or by contacting them with each other without using any solvent, and then adding a solvent to the resultant. The contact of the tantalum compound with the alkylating agent is beforehand 20 conducted, and subsequently the mixture is brought into contact with an olefin, whereby the trimerization can be carried out. The contact of the tantalum compound with the alkylating agent is conducted in the presence of an olefin, whereby the trimerizing reaction can be started at the same time when the tantalum compound 25 is brought into contact with the alkylating agent. The mixing order of these starting materials is not particularly limited. Preferably, the alkylating agent is added to the tantalum compound.

In the preparation of the catalyst of the invention and

the trimerizing reaction, a solvent is used. Examples of the solvent used herein include aliphatic hydrocarbons such as butane, pentane, hexane, heptane, octane, isooctane, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, cyclooctane, and decalin; aromatic hydrocarbons such as benzene, toluene, xylene, cumene, ethylbenzene, monochlorobenzene, or dichlorobenzene; and halogenated hydrocarbons such as dichloromethane, chloroform, carbon tetrachloride, or dichloroethane. The olefin itself which is the starting material for the trimerizing reaction, or a reaction product olefin such as 1-butene, hexene or octene, can be used as the solvent.

The solvent is preferably an aromatic hydrocarbon, and is more preferably benzene, toluene, xylene, monochlorobenzene, dichlorobenzene or the like. These solvents may be used alone or in the form of a mixture of two or more thereof.

The concentration of the tantalum compound when the catalyst of the invention is prepared is not particularly limited, and is usually from 0.0001 μmol to 100 mmol, preferably from 0.001 μmol to 10 mmol.

In the catalyst of the invention, the amount of the alkylating agent is usually from 0.5 to 4 times by mole, preferably from 0.7 to 3 moles, more preferably from 1 to 2.5 moles in terms of the alkyl group(s) per mol of the tantalum compound. The wording "in terms of the alkyl group(s)" means that a number corresponding to the mole number of the alkyl group(s) which can react with the tantalum compound, and can be represented as the product of the mole number of the alkylating agent per mol of the tantalum compound and the number of the alkyl group(s)

that the alkylating agent has. For example, when the amount of isopropyl lithium is 1 mole per mol of the tantalum compound, the amount in terms of the alkyl group(s) is 1 mole. When the amount of diisopropyl zinc is 1 mole per mol of the compound,
5 the amount in terms of the alkyl group(s) is 2 moles.

The temperature when the catalyst of the invention is prepared is usually from -100 to 250°C, preferably from -78 to 150°C. The time for the preparation is not particularly limited, and is usually from 0 minute to 24 hours.

10 The preparation of the catalyst of the invention and the trimerizing reaction are preferably conducted in an inert gas atmosphere while the contact with water is avoided. Thus, it is preferred that the compounds to be used are sufficiently dried in advance.

15 The thus-prepared catalyst is used to carry out the trimerizing reaction of an olefin. The amount of the catalyst of the invention is not particularly limited, and is usually from 0.001 μ mol to 100 mmol, preferably from 0.01 μ mol to 10 mmol per liter of the solvent.

20 Examples of the olefin which is used as the starting material in the invention include α -olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, or 1-decene; internal olefins such as 2-butene, 2-pentene, 2-hexene, 3-hexene, 2-octene, 3-octene, and
25 4-octene; branched olefins such as isobutylene, 3-methyl-1-butene, 4-methyl-1-pentene, or 2-ethyl-1-hexene; and diolefins such as 1,3-butadiene, isoprene, 1,4-pentadiene, or 1,5-hexadiene.

The catalyst for the present reaction is highly active

and particularly suitable for the trimerizing reaction of ethylene, and makes it possible to yield 1-hexene with a high activity and a high selectivity.

The temperature of the trimerizing reaction in the invention is usually from -100 to 250°C, preferably 150°C or lower, more preferably from 0 to 200°C, even more preferably from 10 to 80°C. The reaction pressure is usually an absolute pressure of from normal pressure to a pressurized pressure, preferably of from normal pressure to 300 MPa, more preferably of from normal pressure to 30 MPa. The reaction time is not particularly limited, and is usually from 0 minute to 24 hours.

The starting material olefin may be continuously supplied to keep the above-mentioned pressure, or may be sealed up at the above-mentioned pressure as the reaction is started. The olefin diluted with nitrogen, argon, helium or the like may be used.

The present reaction can be carried out in a batch-wise manner, semi-continuous manner, or continuous manner. After the end of the reaction, an inactivating agent such as water, an alcohol, hydrochloric acid, or an aqueous sodium hydroxide solution, is added to the reaction solution, thereby terminating the reaction. After completion of the reaction, the inactivated catalyst is removed by a known demineralization treatment such as extraction with water or an aqueous alkaline solution. Thereafter, the desired olefin can be separated by a known operation such as distillation or extraction.

The trimerizing reaction of an olefin is preferably carried out under a reaction condition wherein the water content in the reaction system is 50 moles or less per mole of the tantalum

atom and the amount of molecular oxygen in the reaction system is 10 moles or less per mole of the tantalum atom.

Examples

5 The present invention will be described in more detail by way of the following examples. However, the invention is not limited to these examples.

Example 1

10 Toluene was charged into an autoclave in the atmosphere of ethylene, the pressure of which was normal pressure, so as to set the total amount thereof to 5 mL, and thereto was added 0.8 mL of a solution of 22.4 mg of tantalum pentachloride dissolved in 10 mL of toluene (the amount of tantalum pentachloride: 5
15 μmol). The temperature thereof was then stabilized at 40°C. Thereafter, the pressure of ethylene was increased to 0.6 MPa, and stabilized. Thereinto was charged 13 μL (3.3 μmol) of triisobutylaluminum (manufactured by Tosoh Fine Chemicals Pte Ltd., 0.25 mol/L solution in toluene), and ethylene was caused
20 to react for a time shown in Table 1. The reaction container was cooled to room temperature, and next the pressure was returned to normal pressure. The reaction solution was analyzed by gas chromatography. A solid matter contained in the reaction
25 solution was filtrated off with filter paper. This solid was air-dried and then dried at a reduced pressure. The weight thereof was then measured. The results are shown in Table 1.

Example 2

The reaction operations were carried out in a similar

manner as in Example 1 except using the kind of an alkylating agent, a charged amount thereof and a reaction time shown in Table 1. The results are shown in Table 1. PBAO represents polyisobutylaluminumoxane.

5

Examples	1	2
TaCl ₅ : μ mol	5.0	5.0
Alkylating agent μ mol	TIBA 3.3	PBAO 10.0
Reaction time: hour(s)	0.44	1.5
Reaction temperature: °C	40	40
Components: wt%		
C4	10.3 (99.0)	3.4 (91.2)
C6	84.2 (99.0)	95.4 (98.7)
C8	0.9 (0)	0.0
C10	3.7 (0)	1.2 (0)
C12	0.0	0.0
C14	0.2 (0)	0.0
C16	0.0	0.0
Solid component (PE)	0.7	0.0
Activity: mol/(mol(cat.)-hr)		
1-Butene	190	9
1-Hexene	1034	176
1-Octene	0	0
1-Decene	0	0
1-Dodecene	0	0
1-Tetradecene	0	0
1-Hexadecene	0	0

C4: Butene, C6: Hexene, C8: Octene, C10: Decene, C12: Dodecene, C14: Tetradecene, C16: Hexadecene

The number in parentheses in each column for the components represents the purity of linear α -olefins in the each of the components ((the amount of linear α -olefins/the total amount of isomers of each of the components) $\times 100$)

TIBA: Triisobutylaluminum

PBAO: Polyisobutylaluminumoxane (manufactured by Tosoh Fine

Chemicals Pte Ltd.)

Example 3

Toluene was charged into an autoclave in the atmosphere
5 of ethylene, the pressure of which was normal pressure, so as
to set the total amount thereof to 5 mL, and thereto was added
0.8 mL of a solution of 167.9 mg of tantalum pentachloride
suspended in 15 mL of toluene (the amount of tantalum
pentachloride: 25 μ mol). The temperature thereof was then
10 stabilized at 40°C. Thereafter, the pressure of ethylene was
increased to 0.6 MPa, and stabilized. Thereinto was charged
26 μ L (50 μ mol) of MMAO-3A (modified methylaluminoxane
manufactured by Tosoh Fine Chemicals Pte Ltd., 1.9 mol/L solution
in toluene), and ethylene was caused to react for 0.2 hour. The
15 reaction container was cooled to room temperature, and next the
pressure was returned to normal pressure. The reaction solution
was analyzed by gas chromatography. A solid matter contained
in the reaction solution was filtrated off with filter paper.
This solid was air-dried and then dried at a reduced pressure.
20 The weight thereof was then measured. The results are shown
in Table 2.

Comparative Example 1

The same operations as in Example 3 were carried out except
25 that dimethylzinc was used instead of MMAO-3A and the reaction
was conducted for a reaction time shown in Table 2. The results
are shown in Table 2.

Table 2

	Example 3	Comparative Example 1
TaCl ₅ : μ mol	25	25
Alkylating agent μ mol	MMAO-3A 50	ZnMe ₂ 25
Reaction time: hour(s)	0.2	1.3
Reaction temperature: °C	40	40
Components: wt%		
C4	3.3 (100)	12.3 (98.4)
C6	87.4 (97.4)	76.4 (86.9)
C8	3.1 (3.2)	1.9 (0)
C10	6.2 (0)	3.4 (0)
C12	0.6 (16.7)	0.2 (0)
C14	1.2 (0)	0.0
C16	0.0	0.0
Solid component (PE)	1.4	0.0
Activity: mol/(mol(cat.)-hr)		
1-Butene	33	12
1-Hexene	568	42
1-Octene	0	0
1-Decene	0	0
1-Dodecene	0	0
1-Tetradecene	0	0
1-Hexadecene	0	0

C4: Butene, C6: Hexene, C8: Octene, C10: Decene, C12: Dodecene,
C14: Tetradecene, C16: Hexadecene

The number in parentheses in each column for the components represents the purity of linear α -olefins in the each of the
5 components ((the amount of linear α -olefins/the total amount of isomers of each of the components) \times 100)

MMAO-3A: Modified methylaluminoxane (manufactured by Tosoh Fine Chemicals Pte Ltd.)

10 Example 4

Toluene was charged into an autoclave in the atmosphere of ethylene, the pressure of which was normal pressure, so as to set the total amount thereof to 5 mL, and thereto was added

125 μ L of a solution of 100.3 mg of tantalum pentachloride
suspended in 14 mL of toluene (the amount of tantalum
pentachloride: 2.5 μ mol). The temperature thereof was then
stabilized at 70°C. Thereafter, the pressure of ethylene was
5 increased to 0.6 MPa, and stabilized. Thereinto was charged
67 μ L (1.7 μ mol) of triisobutylaluminum (TIBA manufactured by
Tosoh Fine Chemicals Pte Ltd., 0.025 mol/L solution in toluene),
and ethylene was caused to react for 3 hours. The reaction
container was cooled to room temperature, and next the pressure
10 was returned to normal pressure. The reaction solution was
analyzed by gas chromatography. A solid content contained in
the reaction solution was filtrated off with filter paper. This
solid was air-dried and then dried at a reduced pressure. The
weight thereof was then measured. The results are shown in Table
15 3.

Example 5

The reaction operations were carried out in a similar
manner as in Example 4 except that o-dichlorobenzene was used
20 instead of toluene as the solvent in Example 4. The results
are shown in Table 3.

Comparative Example 2

The reaction operations were carried out in a similar
25 manner as in Example 4 except that dimethylzinc was used instead
of triisobutylaluminum in Example 4. The results are shown in
Table 3.

Table 3

Examples	4	5	Comparative Example 2
TaCl ₅ : μ mol	2.5	2.5	3
Alkylating agent μ mol	TIBA 1.7	TIBA 1.7	ZnMe ₂ 3
Reaction time: hour(s)	3.0	3.0	3.0
Reaction temperature: °C	70	70	70
Solvent	Toluene	o-Dichlorobenzene	Toluene
Components: wt%			
C4	1.1 (100)	1.0 (100)	0.2 (100)
C6	94.4 (99.9)	86.9 (99.8)	96.5 (100)
C8	0.1 (0.0)	0.7 (0.0)	0.1 (100)
C10	4.3 (65.1)	10.8 (50.9)	3.2 (0)
C12	0.0	0.0	0.0
C14	0.0	0.6 (0.0)	0.0
C16	0.0	0.0	0.0
Solid component (PE)	0.0	0.0	0.0
Activity: mol/(mol(cat.)-hr)			
1-Butene	6	8	0
1-Hexene	356	460	100
1-Octene	0	0	0
1-Decene	3	5	0
1-Dodecene	0	0	0
1-Tetradecene	0	0	0
1-Hexadecene	0	0	0

C4: Butene, C6: Hexene, C8: Octene, C10: Decene, C12: Dodecene,
C14: Tetradecene, C16: Hexadecene

The number in parentheses in each column for the components represents the purity of linear α -olefins in the each of the components ((the amount of linear α -olefins/the total amount of isomers of each of the components) $\times 100$)

Industrial Applicability

According to the present invention, a catalyst having a good catalytic activity can be obtained, and an olefin can be trimerized by use of this catalyst.